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## **Dynamics of Changes in Composition and Stability of the Heavy Oil Sampled from the Usinskoye Oil Field as a Result of Formation Treatment with a Sol-Forming EOR System**

**Darya I. Chuikina\***,  
**Tatiana V. Petrenko, Larisa D. Stakhina**  
*Institute of Petroleum Chemistry SB RAS  
4 Akademichesky, Tomsk, 634055, Russia*

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*The paper deals with a sol-forming system for oil recovery enhancement (EOR system) used to increase the rate of heavy oil displacement. The effect of sol-forming EOR system during the heavy oil displacement on the composition and stability of oil sampled from the Usinskoye oil field of Russia is investigated. The composition of a crude oil also plays an important role in changing its stability. The work is aimed to investigate stability of heavy crude oil in regards to asphaltene precipitation. For asphaltene toluene/n-heptane solutions, the aggregation stability of asphaltenes based on change in the optical density with time is investigated via spectrophotometry. SARA analysis is used to characterize the compositions of heavy oils. First, the content of asphaltenes precipitated from the oil samples is determined and then the samples of deasphalted crude oil (maltenes) are analyzed by the method of liquid adsorption chromatography for the purpose to study the composition of oil sampled from the wells before and after their treatment with the sol-forming EOR system. It is found out that the treatment of reservoir crude oil with the sol-forming EOR system results in changes in composition of saturated, aromatic hydrocarbons, resins, and asphaltenes (SARA components) and aggregative stability of produced oil. The results obtained showed that the aggregative stability of heavy oil depends not only on the content of SARA components in the dispersion medium but on the presence of metalloporphyrins in the oil. Metalloporphyrins could act as inhibitors of asphaltene precipitation, which is an additional factor responsible for the stabilization of the oil dispersed system.*

**Keywords:** *EOR methods, sol-forming system, displacement, heavy crude oil, composition, asphaltenes, resins, hydrocarbons, metalloporphyrins, stability, spectrophotometry.*

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## **Динамика изменения состава и устойчивости нефти Усинского месторождения в результате обработки пласта золеобразующей композицией для интенсификации нефтеотдачи**

**Д.И. Чуйкина, Т.В. Петренко, Л.Д. Стахина**  
*Институт химии нефти СО РАН*  
*Россия, 634055, Томск, пр. Академический, 4*

*Чтобы улучшить интенсивность вытеснения тяжелой нефти, используют золеобразующую композицию для увеличения нефтеотдачи (EOR). Исследовано влияние золеобразующей композиции в качестве метода увеличения нефтеотдачи (EOR) при вытеснении тяжелой нефти на состав и устойчивость образцов из Усинского нефтяного месторождения России. Важное влияние на устойчивость нефти оказывает ее состав. Целью исследования является изучение устойчивости тяжелой нефти в отношении осаждения асфальтенов. Агрегационная устойчивость асфальтенов была изучена на основе изменения оптической плотности во времени для растворов асфальтенов в толуоле/н-гептане методом спектрофотометрии, для характеристики состава тяжелых нефтей использовали анализ содержания насыщенных ароматических углеводородов, смол и асфальтенов. Состав образцов нефти из скважин до и после обработки золеобразующей композицией, используемой для увеличения нефтеотдачи, изучали методом жидкостно-адсорбционной хроматографии деасфальтизированной нефти (мальтенов). Предварительно было проведено выделение и определение содержания асфальтенов в образцах нефти. Установлено, что обработка пластовой нефти золеобразующей композицией EOR приводит к изменениям состава компонентов (насыщенных ароматических углеводородов, смол и асфальтенов) и агрегационной устойчивости добываемой нефти. Полученные результаты показали, что агрегационная устойчивость тяжелой нефти зависит не только от содержания насыщенных, ароматических углеводородов, смол и асфальтенов в дисперсионной среде. Дополнительным фактором стабилизации нефтяной дисперсной системы является наличие металлопорфиринов в нефти, которые могут действовать как ингибиторы осаждения асфальтенов.*

*Ключевые слова: методы увеличения нефтеотдачи, золеобразующая композиция, вытеснение, тяжелая нефть, состав, асфальтены, смолы, углеводороды, металлопорфирины, устойчивость, спектрофотометрия.*

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## Introduction

The oil composition changes during production, transportation, and processing of crude oils [1, 2]. It is known that heavy oil is a continuously distributed colloid system with dynamic stability [3]. The effects of compositional changes on asphaltene stability have been investigated for different crude oils, fractionated asphaltenes, and resins with hydrocarbons that act either as asphaltene solvents or flocculating agents. A literature review suggests that much attention is now devoted to the study of the stability of oil dispersed systems, since it plays an important role in the processes of extraction, transport, processing, storage and use of hydrocarbon raw materials [4, 5]. The change in conditions such as reservoir pressure and temperature, as well as its transportation and storage results in unbalance within the system and can cause changes in the stability. Effects of the addition of resins on aggregation and stability of petroleum asphaltenes in hydrocarbon solutions are studied by dynamic light scattering. The average aggregate size was monitored in real time as a function of the concentration of the precipitant (heptane) and resins. It is shown that resins serve as inhibitors for asphaltene aggregation, shifting the onset of aggregation. However, the dependence of the onset on the concentration of resins has a tendency to saturate [6, 7]. In the structuring of oil dispersed systems the focus is on asphaltenes, which affect the stability of colloidal oil structure. A decrease in the stability of the oil dispersed system during the development of the oil field and the extraction of oil is accompanied by the deposition of asphaltene-resin-paraffin deposits, which result in the colmatation of rocks and contamination of downhole equipment. They also hamper the technological processes of transportation of hydrocarbon raw materials. However, it is important to accelerate the changes in oil stability during deasphalting, deparaffination, crystallization, etc. The colloidal stability of oil systems depends on the composition and content of the dispersed phase and dispersion medium in the oil. To prevent the deposition of asphaltenes, additives of aromatic hydrocarbons, deasphaltisate, resins and special inhibitory substances can be used.

Aromatic hydrocarbons and resins have a positive effect on the resistance of oil to asphaltene deposition [8]. The number of resins should be sufficient to form an adsorption layer on the surface of asphaltenes and stabilize dispersed systems. The presence of a sufficient amount of aromatic hydrocarbons in the dispersion medium has a positive effect on the stability of asphaltenes, since they have a polyaromatic structure. A large number of studies deals with the mechanisms of these processes, since their understanding allows one to reasonably approach to the choice of physico-chemical impacts on the reservoir, aimed at enhancing oil recovery. The composition of oils plays an important role in changing the stability of oil in the formation, when partial dissolution of some components in water and enrichment of oil with resin-asphaltene substances (RAS) and newly formed ones due to chemical and biochemical oxidation take place. The application of enhanced oil recovery (EOR) methods can also have an impact on oil characteristics. The chemical reagents used in the course of EOR methods application can have an inhibitory effect on the deposition of asphaltenes in a crude oil. The changes in the composition of the high-viscosity heavy oil from the Usinskoye oil field due to the formation treatment with the oil-displacing composition containing synthetic surfactant were studied in [9, 10]. The aim of this work was to study changes in the composition and stability of heavy oil from the Usinskoye field during its production using a sol-forming system used for the enhanced oil recovery (EOR system). The composition of oil samples

was investigated and optical absorption spectra of asphaltenes isolated from the oil samples were recorded. During asphaltene precipitation these spectra were analyzed in the visible region via electronic spectrophotometry.

### Experimental

**Oil samples.** Oil samples from well No. 12XX of Permo-Carbon deposit of the Usinskoye oil field (Komi Republic, Russia) and those before and after injection of the sol-forming EOR system were taken as subjects of investigation.

**EOR system.** In the Usinskoye oil field, the sol-forming EOR system was injected by the technology developed in the IPC SB RAS. The sol-forming EOR system (S) is based on aluminum chloride and carbamid [11, 12]. The sol-forming EOR-system (S) injected into the reservoir generates a sol (gel) and CO<sub>2</sub>, which results in a redistribution of filtration flows, a decrease in water cut, and an increase in oil production.

**SARA composition analysis.** The content of the main SARA components (saturated and aromatic hydrocarbons, resins, asphaltenes) was determined in the oil samples. To separate asphaltenes, the weighed obtained samples were diluted with a 40-fold excess of hexane and left for 24 hours [13]. A precipitate of asphaltene was removed by filtration through a paper filter and then washed with hexane from co-precipitated resins and hydrocarbons (malthenes). Malthenes were separated by chromatography in a Soxhlet apparatus on silica gel. They were successively eluted with hexane in order to desorption saturated and aromatic hydrocarbons (SA-HCs), and with an alcohol: chloroform mixture (7:93) to isolate the resins [14].

**GC-MS analysis.** The individual and group composition of compounds in malthenes was analyzed by gas chromatography-mass spectrometry (GC-MS) using a Thermo Scientific DFS magnetic-mass spectrometer (Germany). The data of NIST Mass Spectral Library were used to identify compounds: alkanes, naphthenic (Napht HCs) and aromatic (Aromatic HCs) hydrocarbons, heterorganic compounds (HOC). Ionization was carried out by electron impact; ionizing electron energy was 70 eV; temperature of the ionization chamber was +250 °C; mass spectra were recorded in the range of 50-500 atomic mass unit; spectrum sweep duration was 1 s.

**Porphyrins analysis.** Metalloporphyrins were analyzed by the method of elution chromatography on aluminum oxide IV degree of activity. The extraction of fractions was carried out sequentially first with carbon tetrachloride and then benzene. The metalloporphyrins were examined with the aid of UV/VIS-spectrophotometer 'UVIKON 943' (KONTRON INSTRUMENTS, Italy), using the adsorption band intensity in the visible region of the spectrum (550 nm for nickel porphyrin and 570 nm for vanadium porphyrin).

**Stability.** The aggregative stability of oil samples was measured by the method of spectrophotometry using an UVIKON 943 instrument programmed to automatically record the changes in optical density (D) over time [15]. The n-hexane in a precipitation/solvent ratio of 3:1 was added to a solution of crude oil in toluene (3 wt% concentration). The resulted mixture was rapidly mixed and the kinetic curve of the change in optical density over time was recorded. The optical density of the solutions was measured at a wavelength of 650 nm in a 1 cm sealed cell for 150 minutes. The optical density of oil solutions was also measured at a wavelength of 500 nm to calculate the specific coefficient of light absorption  $K_{500}$  (dm<sup>3</sup>/g • cm) according to the formula:

$$K_{500} = D_{500}/C \cdot l$$

where:  $D_{500}$  is the optical density of the oil solution at a wavelength of 500 nm;

- $C$  is the concentration of the oil solution in toluene, g/dm<sup>3</sup>;
- $l$  is the thickness of the cell, cm;
- $K_{500}^1$  is the specific light absorption coefficient of the initial oil solution in toluene, dm<sup>3</sup>/g•cm;
- $K_{500}^2$  is the specific light absorption coefficient of the oil solution after addition of hexane and deposition of asphaltenes, dm<sup>3</sup>/g•cm;
- and  $K_{500}^1/K_{500}^2$  is the ratio of specific indicators of light absorption.

### Results and discussion

In [6, 15] was shown that the one of the main factors affecting the colloidal stability of crude oil is the high content of aromatic hydrocarbons and resins. The resistance of oils to asphaltene precipitation depends on the resin content and the steric position of resins relative to asphaltenes. The stabilization of asphaltenes occurs when resins are adsorbed by aromatic ‘heads’ on the surface of asphaltenes, while the aliphatic part of resins, so-called ‘tails’, being in the dispersion phase form a stabilization layer. An additional condition is the chemical affinity of the aliphatic part of resins and a dispersion medium [16].

Table 1 shows the component composition of oil sampled from the wells No.12XX before and after treatment with the sol-forming system S. The total content of saturated and aromatic hydrocarbons (SA-HCs) and resin+asphaltene substances (RAS) in the initial oil sampled from the well No. 12XX was, 71.5 and 28.5 wt%, respectively. The resin/asphaltenes (2.8) and RAS/SA-HCs components (0.4) ratios make it possible to evaluate the aggregative stability [17] (Table 1).

Before the treatment, the content of aromatic hydrocarbons in the initial oil samples was 63% rel., while that of saturated hydrocarbons 33% rel., where 26% were naphthenic hydrocarbons and 7% – alkanes (Fig. 1).

In Figure 2 are shown the curves of the changes in optical density for oil solutions, which make it possible to evaluate the stability to precipitation of asphaltenes in samples from the well No. 12XX before and after injection of the gelling S composition.

At the initial stage after the addition of n-hexane, a structural rearrangement of the system is observed, which consists in the flocculation of asphaltenes. The optical density increases due to an increase in the contribution of growing particles to the absorption of light. The flocculation is

Table 1. Composition of oil samples taken out from the well No. 12XX before and after treatment with the sol-forming system S

Oil sample. Sampling date	Content, wt%			Resins/ Asphaltenes ratio	RAS / SA-HCs ratio
	SA-HCs	Resins	Asphaltenes		
Initial oil	71.5	21.0	7.5	2.8	0.4
1 month later	68.2	23.5	8.3	2.8	0.5
3 months later	63.5	26.6	9.6	2.8	0.6
5 months later	65.9	24.3	9.8	2.5	0.5
11 months later	75.0	18.2	6.8	2.7	0.3

completed, asphaltene particles precipitate, as can be seen from the decrease in the optical density of the solution as a function of time (Fig. 2).

The injection of the sol-forming system S resulted in a redistribution of the filtration flows within the formation, which promoted the involvement of heavier high-resin oil into the extraction. The one, three and five months later, the content of RAS in the oil composition has increased from 28.5 to 31.8 – 36.2 wt%, while the resins/asphaltenes ratio remained unchanged. The ratio of RAS to SA-HCs components increased from 0.4 to 0.5 – 0.6 (Table 1). The content of aromatic hydrocarbons decreased by 7% rel., while that of saturated hydrocarbons increased by 2% rel. In particular, the content in naphthenic HCs increased by 6% and that in alkanes decreased by 4% (Fig. 1). It is evident from Fig. 2 (curves 3 and 4) that the oil sampled 3 and 5 months after the injection of the system S have a higher resistance to asphaltene precipitation. This resulted in an increase in the aggregative oil stability.

Eleven months after treatment, the ratio of resin-asphaltene components to hydrocarbons (RAS / SA-HCs) decreased to 0.3 (Table 1). The content of aromatic hydrocarbons decreased by 15% rel.,

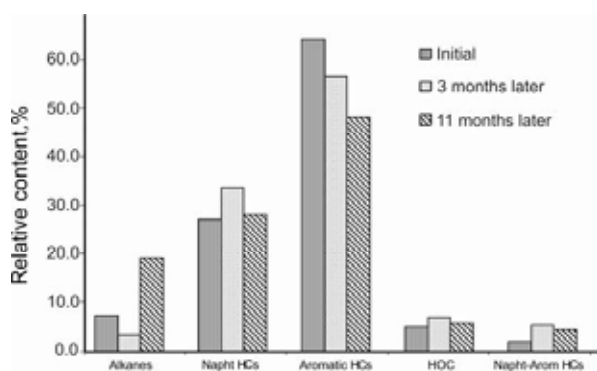


Fig. 1. Group composition of the saturated and aromatic hydrocarbons for oil samples from the well No. 12XX, sampled at various time periods (before and after treatment with the sol-forming system S)

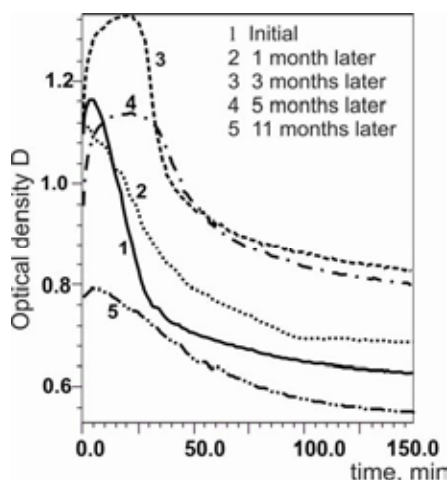


Fig. 2. Changes in the optical density of the solution during asphaltene precipitation from oil samples: well No. 12XX (the sol-forming system S)

while the content of saturated hydrocarbons increased by 12% rel. as compared to the initial oil sample. In particular, the content in naphthenic HCs increased by 1% and that in alkanes by 11% (Fig. 1). The combination of these indicators affected the stability of the oil. Hence, the oil sample exhibited the lowest optical density, and thus, the lowest stability (Fig. 2, curve 5).

This confirms the dependence of the oil stability on the content of natural stabilizers represented by resins. It was found out in [15] that the ratio of the specific light absorption coefficient of the initial oil solution ( $K_{500}^1$ ) to that of the solution after asphaltene precipitation ( $K_{500}^2$ ) correlates well with the resins/asphaltenes ratio. So, the higher the fraction of resins and lower the value of  $K_{500}^1/K_{500}^2$ , the higher is oil stability.

Based on the spectral data in the UV visible region of spectrum the ratios of specific light absorption coefficients ( $K_{500}^1/K_{500}^2$ ) for the oil samples from the Usinskoye oil field were calculated. Oil samples from the well No. 12XX sampled 3 and 5 months later after treatment are characterized by the minimum  $K_{500}^1/K_{500}^2$  ratio, 1.45 and 1.48, respectively, which indicates its higher stability.

It was shown in [18] that the introduction of a concentrate of vanadylporphyrins into the model mixture results in an increase in the aggregative stability of the system obtained. It is known that one of the important factors affecting the stability of oil is the nature of the asphaltenes themselves. Oil vanadylporphyrins are close in size and molecular weight to the structures of the light fraction of asphaltenes, so they act as dispersants, preventing agglomeration of asphaltene nanoaggregates and formation of flocculi [19]. Vanadylporphyrins inhibit the asphaltene precipitation due to multiple intermolecular interactions. Hence, the addition of the concentrate of vanadylporphyrins to oil resins increases their effectiveness as asphaltene precipitation inhibitors, which is of practical importance. It has been shown that with an increase in the content of vanadilporphyrins in the resins of heavy oils, their ability to precipitate asphaltenes decreases. The addition of the concentrate of vanadylporphyrins to petroleum resins increases their effectiveness as an inhibitor of asphaltene precipitation, which has practical prospects in technological processes of production of extra-viscous oil using hydrocarbon solvents based on light alkanes.

Metalloporphyrins have been identified in the oil samples from the Usinskoye oil field. They contain large concentrations (170 – 310 nmol/g) of vanadyl complexes [20]. Comparison of data on stability with those on the content of metal complexes in oil samples showed a relationship between these parameters. Hence, a decrease in the content of porphyrins is proportional to a decrease in aggregative stability ( $K_{500}^1/K_{500}^2$ ) of oil sampled 1 month after treatment with the sol-forming system S (see Fig. 3). Thus, a study of the samples of heavy high-viscosity oil from the Usinskoye oil field has been shown that in the case of field application the aggregative stability of oils increases with increasing content in metalloporphyrins.

Over time (3 and 5 months after the injection of the system S) the content of metalloporphyrins in the samples increased by 1.3 -1.8 times. The stability of the oil was observed also increased.

## Conclusions

The results obtained showed that the aggregative stability of crude oil is affected not only by the content of aromatic hydrocarbons and resins in the dispersion medium. An additional factor in stabilizing the oil dispersed system is the presence of metalloporphyrins in the oil, which can act as inhibitors of asphaltene precipitation. The ratio of the specific light absorption coefficient of the

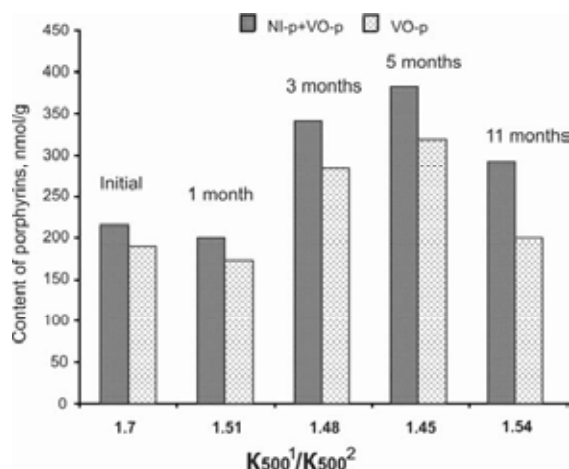


Fig. 3. Dependence of the content of porphyrins and the stability ( $K_{500}^1/K_{500}^2$  ratio) for oil samples from the well No. 12XX, sampled at various time periods (before and after treatment with the sol-forming system S)

initial oil solution ( $K_{500}^1$ ) to that of the solution after asphaltene precipitation ( $K_{500}^2$ ) makes it possible to rapidly evaluate the oil stability. The selection of the necessary minimum high-performance additives of asphaltene precipitation inhibitors optimizes the processes of super-viscous heavy oil production.

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